



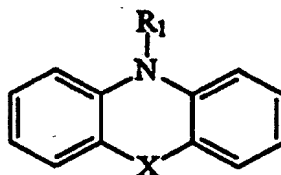
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: DYE TRANSFER INHIBITION SYSTEM CONTAINING A PEROXIDASE/ACCELERATOR SYSTEM

## (57) Abstract

Dye transfer inhibiting systems are disclosed, comprising an enzyme exhibiting peroxidase activity, a hydrogen peroxide source, an additional oxidizable substrate, and an accelerator preferably having formula (I), wherein X is S or O and R<sub>1</sub> is -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, or -CH<sub>2</sub>CH<sub>2</sub>COOH. Detergent compositions containing the dye transfer inhibition system and typical detergent ingredients are also disclosed. More effective and efficient dye transfer inhibition of fugitive dyes is achieved by using the dye transfer inhibition system as a detergent additive or in a detergent composition matrix.



(I)

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- 1 -

## DYE TRANSFER INHIBITION SYSTEM CONTAINING A PEROXIDASE/ACCELERATOR SYSTEM

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### FIELD OF THE INVENTION

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The present invention relates to a dye transfer inhibition system and detergent compositions containing said dye transfer inhibition system which inhibit the transfer of dye from a dyed fabric to another fabric during washing. The dye transfer inhibition system comprises a peroxidase enzyme, a hydrogen peroxide source, and an accelerator, preferably a phenothiazine or phenoxazine accelerator.

15

### BACKGROUND OF THE INVENTION

One of the most persistent and troublesome problems arising during modern fabric laundering operations is the tendency of some colored fabrics to release dye ("fugitive dye") into the laundering solutions. The dye is then transferred onto other fabrics being washed therewith.

20

One way of overcoming this problem would be to bleach the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

25

Suspended or solubilized dyes can to some degree be oxidized in solution by employing known bleaching agents.

GB 2 101 167 describes a stable liquid bleaching composition containing a hydrogen peroxide precursor which is activated to yield hydrogen peroxide on dilution.

30

However, it is important at the same time not to bleach the dyes actually remaining on the fabrics, that is, not to cause color damage.

U.S. Patent 4,077,768 describes a process for inhibiting dye transfer by the use of an oxidizing bleaching agent together with catalytic compounds such as iron porphins.

U.S. Patent Application 421,414 describes peroxidases and oxidases utilized for the oxidation of organic or inorganic substances, including colored substances.

35

A dye transfer inhibiting composition comprising an enzymatic system capable of generating hydrogen peroxide and iron catalysts has been disclosed in copending EP Patent Application 91202655.6, filed October 9, 1991.

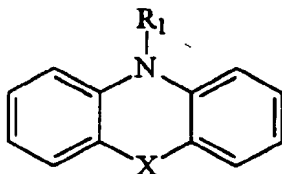
EP 424 398-A describes a detergent additive capable of exerting a bleaching effect comprising a peroxidase. The additive further comprises one or more enzymes, particularly a lipase, protease, amylase or a cellulase.

Peroxidase enzymes are bleaching enzymes which have been proposed for dye transfer inhibition. It has been determined that to achieve good dye bleaching, particularly at high pH levels, e.g., levels above about 8 or 9, an accelerator is required for the peroxidase enzyme. It has now been surprisingly found that the efficiency of peroxidases in terms of dye transfer inhibition, particularly at pH above about 9, is considerably enhanced by using an accelerator, preferably a phenothiazine or phenoxazine accelerator together with the peroxidase. It is therefore an object of the present invention to provide dye transfer inhibition systems or detergent compositions containing such dye transfer inhibition system which exhibit optimum dye transfer inhibition in wash solutions by using said peroxidase in conjunction with a phenothiazine accelerator.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

## SUMMARY OF THE INVENTION

The present invention provides a dye transfer inhibition system comprising an effective amount of: an enzyme exhibiting peroxides activity; a hydrogen peroxide source selected from the group consisting of hydrogen peroxide, a hydrogen peroxide precursor and an enzymatic system capable of generating hydrogen peroxide; and an accelerator. The accelerator comprises an organic chemical compound consisting of at least two aromatic rings of which aromatic rings at least one is substituted with one or more of the following atoms: nitrogen, oxygen and sulfur; and which aromatic rings may furthermore be fused rings. Preferably, the accelerator is a compound having the formula:



wherein X is S or O, and R<sub>1</sub> is -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, or -CH<sub>2</sub>CH<sub>2</sub>COOH.

In another aspect, the present invention encompasses detergent compositions comprising the dye transfer inhibition system set forth above together with typical

detergent ingredients including a detergent surfactant, detergent builder and other detergent adjuncts.

### DETAILED DESCRIPTION OF THE INVENTION

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The dye transfer inhibition systems herein contain an enzyme exhibiting peroxidase activity, a hydrogen peroxide source, and an accelerator as essential ingredients.

#### PEROXIDASES

10

The peroxidases which may be employed in the dye transfer inhibition systems and detergent compositions of the present invention may be isolated from and are producible by plants (e.g. horseradish peroxidase) or microorganisms such as fungi or bacteria. Some preferred fungi include strains belonging to the subdivision Deuteromycotina, class Hyphomycetes, e.g. Fusarium, Humicola, Trichoderma, Myrothecium, Verticillium,  
15 Arthromyces, Caldariomyces, Ulocladium, Embellisia, Cladosporium or Dreschlera, in particular Fusarium oxysporum (DSM 2672), Humicola insolens, Trichoderma reesi, Myrothecium verrucana (IFO 6113), Verticillium alboatrum, Verticillium dahliae, Arthromyces ramosus (FERM P-7754), Caldariomyces fumago, Ulocladium chartarum, Embellisia allior Dreschlera halodes.

20

Other preferred fungi include strains belonging to the subdivision Basidiomycotina, class Basidiomycetes, e.g. Coprinus, Phanerochaete, Coriolus or Trametes, in particular Coprinus cinereus f. microsporus (IFO 8371), Coprinus macrorhizus, Phanerochaete chrysosporium (e.g. NA-12) or Coriolus versicolor (e.g. PR4 28-A).

25

Further preferred fungi include strains belonging to the subdivision Zygomycotina, class Mycoraceae, e.g. Rhizopus or Mucor, in particular Mucor hiemalis.

Some preferred bacteria include strains of the order Actinomycetales, e.g. Streptomyces spheroides (ATTC 23965), Streptomyces thermoviolaceus (IFO 12382) or Streptoverticillium verticillium ssp. verticillium.

30

Other preferred bacteria include Bacillus pumilus (ATCC 12905), Bacillus stearothermophilus, Rhodobacter sphaeroides, Rhodomonas palustri, Streptococcus lactis, Pseudomonas putrefaciens (ATCC 15958), Pseudomonas fluorescens (NRRL B-11) or Myxococcus virescens.

35

Other potential sources of useful peroxidases are listed in B.C. Saunders et al., op. cit., pp. 41-43.

Methods of producing enzymes to be used according to the invention are described in the art, cf. for example FEBS Letters 1625, 173(1), Applied and Environmental

Microbiology, Feb. 1985, pp. 273-278, Applied Microbiol. Biotechnol. 26, 1987, pp. 158-163, Biotechnology Letters 9(5), 1987, pp. 357-360, Nature 326, 2 April 1987, FEBS Letters 4270, 209(2), p. 321, EP 179 486, EP 200 565, GB 2 167 421, EP 171 074, and Agric. Biol. Chem. 50(1), 1986, p. 247.

5 In general, enzymes exhibiting peroxidase activity which are useful in the dye transfer inhibition system of the present invention are set forth in U.S. Patent 5,273,896 (Pedersen et al), issued December 28, 1993, incorporated herein by reference.

Particularly preferred peroxidases are those which are active at the typical pH of washing liquors, i.e. at a pH of 6.5-10.5, preferably 7.0-10.5, and most preferably 7.5-10.5. Such enzymes may be isolated by screening for the relevant enzyme production by alkalophilic microorganisms, e.g. using the ABTS assay described in R.E. Childs and W.G. Bardsley, Biochem. J. 145, 1975, pp. 93-103.

Other preferred peroxidases are those which exhibit a good thermostability as well as a good stability towards commonly used detergent components such as non-ionic, cationic, or anionic surfactants, detergent builders, phosphate etc.

Another group of useful peroxidases are haloperoxidases, such as chloro- and bromoperoxidases.

The peroxidase-enzyme may furthermore be one which is producible by a method comprising cultivating a host cell transformed with a recombinant DNA vector which carries a DNA sequence encoding said enzyme as well as DNA sequences encoding functions permitting the expression of the DNA sequence encoding the enzyme, in a culture medium under conditions permitting the expression of the enzyme and recovering the enzyme from the culture.

A DNA fragment encoding the enzyme may, for instance, be isolated by establishing a cDNA or genomic library of a microorganism producing the enzyme of interest, such as one of the organisms mentioned above, and screening for positive clones by conventional procedures such as by hybridization to oligonucleotide probes synthesized on the basis of the full or partial amino acid sequence of the enzyme, or by selecting for clones expressing the appropriate enzyme activity, or by selecting for clones producing a protein which is reactive with an antibody against the native enzyme.

Once selected, the DNA sequence may be inserted into a suitable replicable expression vector comprising appropriate promotor, operator and terminator sequences permitting the enzyme to be expressed in a particular host organism, as well as an origin of replication, enabling the vector to replicate in the host organism in question.

35 The resulting expression vector may then be transformed into a suitable host cell, such as a fungal cell, preferred examples of which are a species of Aspergillus, most preferably Aspergillus oryzae or Aspergillus niger. Fungal cells may be transformed by a

process involving protoplast formation and transformation of the protoplasts followed by regeneration of the cell wall in a manner known per se. The use of Aspergillus as a host microorganism is described in EP 238,023 (of Novo Industri A/S), the contents of which are hereby incorporated by reference.

5 Alternatively, the host organisms may be a bacterium, in particular strains of Streptomyces and Bacillus, or E. coli. The transformation of bacterial cells may be performed according to conventional methods, e.g. as described in T. Maniatis et al., Molecular Cloning: A Laboratory Manual, Cold Spring Harbor, 1982.

10 The screening of appropriate DNA sequences and construction of vectors may also be carried out by standard procedures, cf. T. Maniatis et al., op. cit.

The medium used to cultivate the transformed host cells may be any conventional medium suitable for growing the host cells in question. The expressed enzyme may conveniently be secreted into the culture medium and may be recovered therefrom by well-known procedures including separating the cells from the medium by centrifugation or  
15 filtration, precipitating proteinaceous components of the medium by means of a salt such as ammonium sulphate, followed by chromatographic procedures such as ion exchange chromatography, affinity chromatography, or the like.

The screening of appropriate DNA sequences and construction of vectors may also be carried out by standard procedures, cf. T. Maniatis et al., op. cit.

20 The medium used to cultivate the transformed host cells may be any conventional medium suitable for growing the host cells in question. The expressed enzyme may conveniently be secreted into the culture medium and may be recovered therefrom by well-known procedures including separating the cells from the medium by centrifugation or filtration, precipitating proteinaceous components of the medium by means of a salt such  
25 as ammonium sulphate, followed by chromatographic procedures such as ion exchange chromatography, affinity chromatography, or the like.

At the beginning or during the process,  $H_2O_2$  may be added, e.g. in an amount of 0.001-5 mM, particularly 0.01-1 mM. When using *Coprinus* peroxidase, 0.01-0.25 mM  $H_2O_2$  is preferred, and with *B. pumilus* peroxidase 0.1-1 mM  $H_2O_2$ .

30 The hydrogen peroxide may be added as hydrogen peroxide or a precursor thereof, preferably a perborate or percarbonate. The level of hydrogen peroxide precursor that can be used is dependent on the specific properties of the peroxidase chosen, e.g. *Coprinus* peroxidase should be applied in a detergent composition which contains less than 5% perborate.

35 In the process of this invention, it may be desirable to utilize an enzymatic process for hydrogen peroxide formation. Thus, the process according to the invention may additionally comprise adding an enzymatic system (i.e. an enzyme and a substrate therefor)

which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process.

One such category of hydrogen peroxide generating systems comprises enzymes which are able to convert molecular oxygen and an organic or inorganic substrate into hydrogen peroxide and the oxidized substrate respectively. These enzymes produce only low levels of hydrogen peroxide, but they may be employed to great advantage in the process of the invention as the presence of peroxidase ensures an efficient utilization of the hydrogen peroxide produced.

Preferred hydrogen peroxide-generating enzymes are those which act on cheap and readily available substrates which may conveniently be included into detergent compositions. An example of such a substrate is glucose which may be utilized for hydrogen peroxide production by means of glucose oxidase. Suitable oxidases include those which act on aromatic compounds such as phenols and related substances, e.g. catechol oxidases, laccase. Other suitable oxidases are urate oxidase, galactose oxidase, alcohol oxidases, amine oxidases, amino acid oxidase, amyloglucosidase, and cholesterol oxidase.

The preferred enzymatic systems are alcohol and aldehyde L-amino acid oxidases.

The more preferred systems for granular detergent application would have solid alcohols, e.g. glucose whose oxidation is catalysed by glucose oxidase to glucuronic acid with the formation of hydrogen peroxide.

The more preferred systems for liquid detergent application would involve liquid alcohols which could also act as, for example, solvents. An example is ethanol/ethanol oxidase.

The quantity of oxidase to be employed in compositions according to the invention should be at least sufficient to provide a constant generation of 0.01 to 10 ppm AvO per minute in the wash. For example, with the glucose oxidase, this can be achieved at room temperature and at pH 6 to 11, preferentially 7 to 9 with 50-5000 U/l glucose oxidase, 0.005 to 0.5 % glucose under constant aeration.

The addition of another oxidisable substrate for the peroxidase at the beginning or during the washing and/or rinsing process may enhance the dye transfer inhibitory effect of the peroxidase employed. This is thought to be ascribable to the formation of short-lived radicals or other oxidized states of this substrate which participate in the bleaching or other modification of the colored substance. Examples of such oxidisable substrates are metal ions, e.g.  $Mn^{++}$ , halide ions, e.g. chloride or bromide ions, or organic compounds such as phenols, e.g. p-hydroxycinnamic acid or 2,4-dichlorophenol. Other examples of phenolic compounds which may be used for the present purpose are those given in M. Kato and S. Shimizu, Plant Cell Physiol. 26(7), 1985, pp. 1291-1301 (cf. Table 1 in



particular) or B.C. Saunders et al., op. cit., p. 141 ff. The amount of oxidisable substrate to be added is suitably between about 1  $\mu$ M and 1 mM.

In the process of the invention, the peroxidase will typically be added as a component of a detergent composition and may be added in an amount of 0.01 - 100 mg enzyme per liter of wash liquid. As such, it may be included in the detergent composition in the form of a non-dusting granulate, a liquid, in particular a stabilized liquid, or a protected enzyme. Non-dusting granulates may be produced, e.g. as disclosed in US 4,106,991 and 4,661,452 (both to Novo Industri A/S) and may optionally be coated by methods known in the art. Liquid enzyme preparations may, for instance, be stabilized by adding a polyol such as propylene glycol, a sugar or sugar alcohol, lactic acid or boric acid according to established methods. Other enzyme stabilizers are well known in the art. Protected enzymes may be prepared according to the method disclosed in EP 238,216. The detergent composition may also comprise one or more substrates for the peroxidase. Usually, the pH of a solution of the detergent composition of the invention will be preferably from 7-12, especially from 7.5 to 9.5. The wash pH is dependent on the peroxidase chosen, e.g. Coprinus peroxidase should be applied in a wash pH below 9.5.

#### ACCELERATORS

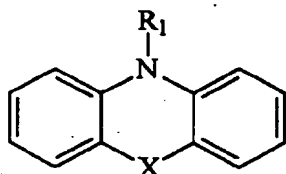
The present invention relates to the use of chemical compounds for enhancing the activity of peroxidase enzymes or peroxidase acting compounds. Accordingly, the invention provides an agent capable of enhancing the effect of a peroxidase enzyme or a peroxidase acting compound, in the following accelerator (hereinafter also referred to as an enhancing agent).

Contrary to the accelerators known and previously described, the accelerators of this invention are capable of acting at alkaline conditions, i.e., at pH levels above about 8. This feature allows the accelerators of the invention to be implemented into various processes including laundering of fabrics.

Basically, the accelerator is an organic chemical compound consisting of at least two aromatic rings of which aromatic rings at least one is substituted with one or more of the following atoms : nitrogen, oxygen and sulfur; and which aromatic rings may furthermore be fused rings.

5

The preferred dye transfer inhibition systems and detergent compositions of the invention herein contain a phenothiazine or phenoxazine accelerator of the formula:

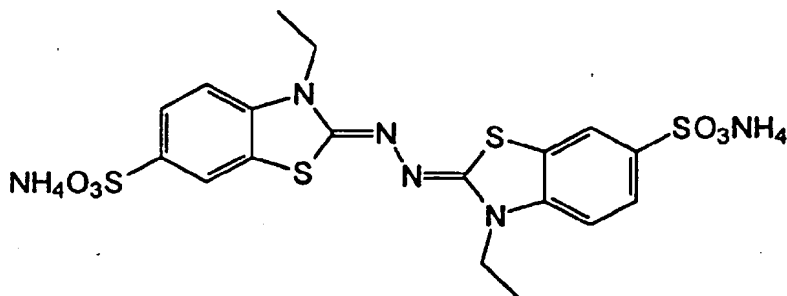


wherein X is S or O, R<sub>1</sub> is -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, or -CH<sub>2</sub>CH<sub>2</sub>COOH. Preferred of the above accelerators is 10-phenothiazinepropionic acid, i.e., wherein R<sub>1</sub> is -CH<sub>2</sub>CH<sub>2</sub>COOH. The accelerator is present at a level of from about 0.01% to about 5%, preferably from about 0.1% to about 0.5%, by weight.

The phenothiazine accelerators are synthesized from 10-H-phenothiazine and are commercially available from Aldrich Chemical.

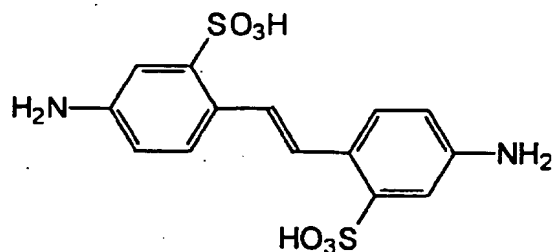
As compared to other dye transfer inhibition systems, the peroxidase-phenothiazine accelerator dye transfer inhibition system provide greater efficiencies with respect to bleaching fugitive dyes in wash water solutions. The dye transfer inhibition systems of the invention hereof provide good dye transfer inhibition performance with, e.g., about 50 to 75% less peroxidase when compared to the dye transfer inhibition performance of similar systems which lack the phenothiazine accelerator.

Other preferred accelerators not in the phenothiazine or phenoxazine classes are accelerators of the formula:



ABTS [2,2'-Azinobis(3-ethyl benzo thiazoline-6-sulfonic acid ammonium salt)]

25



4,4'-Diaminostilbene-2,2'-disulfonic acid

Naturally occurring peroxidase enzymes typically show low activity against most common substrates at pH above about 9. Thus, peroxidase-based dye transfer inhibition (DTI) systems are ineffective in most detergent matrices where pH levels can range from about 9.5 to 10.5 and as high as about 11. The phenothiazine accelerators of the invention herein have been identified as efficient peroxidase accelerators even at pH levels above about 10. This allows for the formulation of DTI systems which are effective at high pH levels and which contain naturally occurring peroxidases and nature-identical peroxidases produced by genetic engineering.

Although not wishing to be bound by theory, it is believed that the accelerator appears to be reversibly oxidized and reduced back to the original compound allowing for low levels of the accelerator to be used. The reversibility appears to be the result of a relatively stable radical cation countered on the nitrogen atom. For 10-phenothiazine propionic acid, the radical cation could be stabilized by the formation of an intramolecular ion pair with the ionized propionic acid moiety.

The levels and ratios of the active components of the DTI system, i.e., hydrogen peroxide, peroxidase enzyme, and phenothiazine accelerator, can have an effect on the performance of the system. For optimal performance, the DTI system contains from about 50 $\mu$ M to about 500 $\mu$ M hydrogen peroxide; from about 0.05 PODU/mL to about 5 PODU/mL peroxidase; and from about 5 $\mu$ M to about 50 $\mu$ M phenothiazine accelerator. The weight ratio of peroxidase to accelerator is preferably from about 1:20 to about 1:200.

In detergent compositions containing the DTI systems wherein a fixed level of hydrogen peroxide in the wash solution is about 100 $\mu$ M, the level of peroxidase is from about 0.05 to about 2 PODU, preferably about 0.1 to about 1 PODU, and the level of phenothiazine accelerator is from about 0.01 to about 1%, preferably from about 0.05 to about 0.2%, by weight.

### 30 DETERGENT ADJUNCTS

The present invention herein also pertains to detergent compositions which contain the dye transfer inhibition system herein and typical detergent components in the usual amounts. Thus, organic surfactants anionic, nonionic, ampholytic, or zwitterionic or less usually cationic and mixtures thereof, may be present. Suitable surfactants are well known  
5 in the art and an extensive list of such compounds is given in US Pat. No. 3,717,630 and in US patent application Ser. No. 589,116.

Detergent compositions useful in the present invention contain from 1 to 95%, preferable from 5 to 40% of a nonionic, anionic, zwitterionic, or mixtures thereof. Detergency builders, whether inorganic or organic, phosphatic or not, water-soluble or  
10 insoluble, and other water-soluble salts may be present, and salts of this sort may be employed whether organic detergents are present or not. A description of suitable builders is given in US Pat. No. 3,936,537 and in US patent application Ser. No. 589,116. Detergent builders are present from 0 to 50%, preferably from 5 to 40%.

Other components used in detergent compositions may be employed, such as suds  
15 boosting or depressing agents, enzymes and stabilizers or activators, soil-suspending agents soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and perfumes.

These components, particularly the enzymes, optical brighteners, coloring agents, and perfumes, should preferably be chosen such that they are compatible with the bleach  
20 component of the composition.

The detergent compositions according to the invention can be in liquid, paste or granular forms. The enzyme may be formulated in any convenient form, e.g. as a powder or liquid. The enzyme may be stabilized in a liquid by inclusion of enzyme stabilizers. Liquid detergents may further include stabilized hydrogen peroxide precursors.

25 Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of  
30 sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

35 The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20°C to 60°C. The pH of the treatment solution is preferably from 7 to 12, especially from 7 to 9.5.

#### 5 OPTIONAL INGREDIENTS

The present compositions will typically include optional ingredients that normally form part of detergent compositions. Antiredeposition and soil suspension agents, optical brighteners, bleaches, bleach activators, suds suppressors, anticaking agents, dyes and pigments are examples of such optional ingredients and can be added in varying amounts as desired.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4<sup>1</sup>-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2<sup>1</sup> disulphonate, disodium 4, - 4<sup>1</sup>-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2<sup>1</sup> - disulphonate, disodium 4,4<sup>1</sup> - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2<sup>1</sup> - disulphonate, monosodium 4<sup>1</sup>,4<sup>11</sup> - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4<sup>1</sup> -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2<sup>1</sup> - disulphonate, disodium 4,4<sup>1</sup> -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2<sup>1</sup> disulphonate, disodium 4,4<sup>1</sup> bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2<sup>1</sup> disulphonate and sodium 2(stilbyl-4<sup>11</sup>-(naphtho-1<sup>1</sup>,2<sup>1</sup>:4,5)-1,2,3 - triazole-2<sup>11</sup>-sulphonate.

Any particulate inorganic perhydrate bleach can be used, in an amount of from 3% to 40% by weight, more preferably from 8% to 25% by weight and most preferably from 12% to 20% by weight of the compositions. Preferred examples of such bleaches are sodium perborate monohydrate and tetrahydrate, percarbonate, and mixtures thereof.

Another preferred separately mixed ingredient is a peroxy carboxylic acid bleach precursor, commonly referred to as a bleach activator, which is preferably added in a

prilled or agglomerated form. Examples of suitable compounds of this type are disclosed in British Patent Nos. 1586769 and 2143231 and a method for their formation into a prilled form is described in European Published Patent Application No. 0 062 523. Preferred examples of such compounds are tetracetyl ethylene diamine and sodium 3, 5, 5 trimethyl  
5 hexanoyloxybenzene sulphonate.

Bleach activators are normally employed at levels of from 0.5% to 10% by weight, more frequently from 1% to 8% and preferably from 2% to 6% by weight of the composition.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-  
10 silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable  
15 carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone  
20 suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m<sup>2</sup>/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow  
25 Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight. The incorporation of the suds modifiers is preferably made as separate particulates, and this permits the inclusion therein of other suds controlling materials such as C20-C24 fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene  
30 oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3,933,672.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

$(\text{CH}_3(\text{PEG})_{43})_{0.75}(\text{POH})_{0.25}[\text{T-PO}]_{2.8}(\text{T-PEG})_{0.4}]\text{T}(\text{PO-H})_{0.25}((\text{PEG})_{43}\text{CH}_3)_{0.75}$   
where PEG is  $-(\text{OC}_2\text{H}_4)_n\text{O}-$ , PO is  $(\text{OC}_3\text{H}_6\text{O})$  and T is  $(\text{pOC}_6\text{H}_4\text{CO})$ .

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both ends by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be endcapped by sulphobenzoate groups. However, some copolymers will be less than fully capped and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane 1-2 diol, about 10% by weight ethylene glycol, about 13% by weight of dimethyl sulfoisophthalic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in EPA 311 342.

Certain polymeric materials such as polyvinyl pyrrolidones typically of MW 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include  $\text{Na}_2\text{EDDS}$  and  $\text{Na}_4\text{EDDS}$ . Examples of such preferred magnesium salts of EDDS include  $\text{MgEDDS}$  and

Mg<sub>2</sub>EDDS. The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type.

5 Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Preferably these clays have a cation exchange capacity of at least 50meq/100 gr. Different examples of clays are described in USP 1,400,898. Montmorillonite clays are widely used for this purpose. Certain hectorite clays also provide good softness performance as described in USP 5,019,292. Organic fabric softening agents include the  
10 water-insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919.

The softening system may contain a flocculating agent to improve clay deposition. Useful organic ingredients of said fabric softening systems include high molecular weight  
15 polyethylene oxide materials having a molecular weight of about 300,000 as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 5% to 20%, more preferably from 8% to 15% by weight with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble  
20 tertiary amines or di-long-chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water-soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be  
25 more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

Enzymes other than the specific peroxidase preparation herein can be present in the composition herein, such as proteases, lipases, amylases and cellulases.

The detergent compositions according to the invention can be in liquid, paste or  
30 granular forms. The enzyme may be formulated in any convenient form, e.g. as a powder or liquid. The enzyme may be stabilized in a liquid by inclusion of enzyme stabilizers. Liquid detergents may further include stabilized hydrogen peroxide precursors.

Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents,  
35 i.e. from 550 to 950 g/l, preferably from 650 to 950g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline



earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20°C to 60°C. The pH of the treatment solution is preferably from 7 to 12, especially from 7 to 10.5.

The process and compositions of the invention can also be used as additive during laundry operations.

The following non-limiting examples illustrate the DTI systems and compositions of the present invention. All percentages, parts and ratios used herein are by weight unless otherwise specified.

### EXAMPLES

Detergent compositions of the present invention are as follows:

<u>Component</u>	Example 1	Example 2	Example 3
		<u>Weight %</u>	
C12 Linear Alkylbenzene Sulfonate	10.5	10.3	8.6
Tallow Alkyl Sulfate	--	--	2.6
C14-15Alkyl Sulfonate	6.7	6.6	--
C14-15AE0.3S	1.9	1.9	--
C12-15AE3S	--	--	0.2
Neodol C12-13 alcohol ethoxylate (9)	0.5	0.5	--
Neodol C14-15 alcohol ethoxylate (7)	--	--	5.0
Tallow Alcohol Ethoxylate (11)	--	--	1.3
Zeolite	25.4	26.3	27.2
Na <sub>2</sub> CO <sub>3</sub>	--	26.0	10.7
NaHCO <sub>3</sub>	--	--	7.0
NaCitrate	--	--	10.0
Citric Acid	2.5	--	--
Na Silicate	0.6	0.6	2.0
Na <sub>2</sub> SO <sub>4</sub>	23.3	--	5.0
Protease	0.8	0.3	1.6
Lipase	--	0.3	0.3
CMC	--	--	0.4
Polyacrylate	3.1	3.2	--
Acrylate-maleate copolymer	--	--	4.6
PEG 4000	1.5	1.7	--
Perborate monohydrate	1.0	1.0	0.5
Peroxidase <sup>1</sup>	0.5	0.5	0.3

10-phenothiazine propionic acid (PPT)  
H2O, Miscellaneous

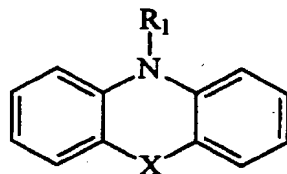
0.1	0.1	0.1
-----Balance-----		

1 - *Coprinus*

5 The above detergent compositions of the present invention provide good dye transfer inhibition of fugitive dyes in wash solutions particularly when compared similar compositions containing no accelerator, i.e., PPT.

## WHAT IS CLAIMED IS:

1. A dye transfer inhibition system characterized in that it comprises an effective amount of:
  - a) an enzyme exhibiting peroxidase activity;
  - b) a hydrogen peroxide source selected from the group consisting of a hydrogen peroxide, hydrogen peroxide precursor, and an enzymatic system capable of generating hydrogen peroxide; and
  - c) an accelerator comprising an organic chemical compound consisting of at least two aromatic rings of which said aromatic rings at least one is substituted with one or more of the following atoms : nitrogen, oxygen and sulfur; and which aromatic rings may furthermore be fused rings.
2. A dye transfer inhibition system according to Claim 1 wherein the the accelerator comprises a phenothiazine or phenoxazine having the formula



wherein X is S or O, R<sub>1</sub> is -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> or -CH<sub>2</sub>CH<sub>2</sub>COOH.

# INTERNATIONAL SEARCH REPORT

International Application No  
**PCT/US 95/04733**

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C11D3/386 C11D3/39 C11D3/28 C11D3/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO, A, 94 12621 (NOVO NORDISK ; SCHNEIDER PALLE (DK); EBDROP SOREN (DK)) 9 June 1994 see claims 23, 28, 42, 43 ---	1, 2
P, X	WO, A, 94 12620 (NOVONORDISK AS ; SCHNEIDER PALLE (DK); ANDERSEN MORTEN BIRKET (DK)) 9 June 1994 see claims 1, 2, 14-16 ---	1
A	WO, A, 93 24618 (NOVONORDISK AS ; WELINDER KAREN GJESING (DK); ANDERSEN MORTEN BIRKE) 9 December 1993 see page 12, line 5 - page 14, line 18; claims 1, 18-21; example 6 -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \* "A" document defining the general state of the art which is not considered to be of particular relevance
- \* "E" earlier document but published on or after the international filing date
- \* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \* "O" document referring to an oral disclosure, use, exhibition or other means
- \* "P" document published prior to the international filing date but later than the priority date claimed

- \* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \* "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \* "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* "&" document member of the same patent family

Date of the actual completion of the international search

27 July 1995

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

**PCT/US 95/04733**

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9412621	09-06-94	AU-B-	7937194	22-05-95
		WO-A-	9511964	04-05-95
		WO-A-	9412620	09-06-94
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WO-A-9412620	09-06-94	WO-A-	9412621	09-06-94
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WO-A-9324618	09-12-93	EP-A-	0652944	17-05-95
		FI-A-	945664	01-12-94
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